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Host Organization: Materials Division
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Assignment:

Development of High-Temperature Shape Memory Alloys

This project will involve research in the development, processing, and characterization of high-temperature shape memory alloys based on NiTiPt alloys. Research will focus on the effect of alloying additions and composition on the martensitic transformation temperature and structure of these alloys and will include development of a ternary Ni-Ti-Pt phase diagram. Also, alloying additions that can replace Pt without significantly lowering the Ms temperature will be investigated. Characterization of these alloys will include detailed analysis by optical, scanning electron, and transmission electron microscopy techniques. Another aspect of this work will focus on the development of processing maps for the determination of appropriate thermophysical processing parameters (temperature, rate, stress, etc.).

Research Summary Submitted by Fellow:

Ti-Ni-Pt-X Shape Memory Alloys for Higher Temperature Applications: Current Status

Overview

Last summer, I was involved in the characterization of twenty-three ternary, quaternary and quinary alloys based on the Ti-Ni-Pt ternary system. These alloys are being investigated to determine their suitability as smart materials for high temperature applications such as automatic actuators, valves, etc. given that they have higher transformation temperatures than all of the other Nitinol-based shape memory alloys studied to date. This summer, I continued to investigate the alloys in this system and many interesting results along with several unexpected complications were discovered. Working closely with Dr. Ron Noebe, Ms. Tiffany Biles and Dr. Anita Garg, who helped in all aspects of this study, along with the oversight of Dr. Mike Nathal, we analyzed a series of binary, ternary and quaternary alloys in order to gain a better understanding of their microstructure-property-processing relationships. The major accomplishments are described in the following.

Major Accomplishments

1. A series of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Pt}_x$ alloys with x ranging from 0 to 50 were analyzed by DSC. The starting materials were disks cut from arc melted buttons that had been given a two-step homogenization treatment at 1050°C , 24h followed by 1200°C , 24h, furnace cooled. The martensite and austenite start, peak and finish temperatures are plotted in Figure 1 where it can be seen that small additions (up to 10%) cause these temperatures to actually drop slightly whereas the larger additions exhibit a linear slope of transformation temperature vs. Pt content. The slope of this response is approximately 25°C per atom percent Pt. This data is useful for selecting particular temperatures where actuation is desired. It should be mentioned that there were some unexpected and unexplained features. For example, the alloy containing 5% Pt substituted for Ni exhibited a reproducible double peak on cooling. The source of this extra peak is uncertain at this time and further work is underway to resolve this apparent anomaly.
2. The second notable finding is that these alloys are very sensitive to interstitial concentrations due to the observation that the austenite (B2) and martensite (B19) phases which exhibit shape memory behavior have low solubilities for interstitials. Consequently, the alloys invariably have at least a small volume fraction of secondary and tertiary phases that contain the rejected interstitials. These include $\text{Ti}_4\text{Ni}_2\text{O}$, $\text{Ti}(\text{CN})$ and a previously unidentified oxide found in "binary" Ti-Pt alloys that contains both Ti and Pt in an approximate ratio of 2. The structure of this latter phase was identified using electron diffraction methods as tetragonal ($a \sim 1.26\text{nm}$, $c \sim 0.66\text{nm}$) with a $4/\text{mmm}$ point group. The space group remains undetermined at this time. Electron energy loss spectroscopy was used to prove that this phase contains oxygen as expected.
3. The third significant observation is that the published Ti-Pt phase diagram is incorrect. Specifically, we discovered at least two new phases with compositions between TiPt and Ti_3Pt where no phases are shown on the phase diagram. One of these was identified using electron diffraction as hexagonal with a $P6_3/\text{mcm}$ space group ($a \sim 0.5\text{ nm}$ and $c \sim 0.8\text{ nm}$) while the other appears to be either trigonal or hexagonal. Unfortunately, the point and space groups of this latter phase are difficult to determine due to the heavy faulting present in the microstructure as well as the very large unit cell ($a \sim 0.8\text{ nm}$ and $c \sim 2.36\text{nm}$). If hexagonal, the unit cell volume is approximately 1.295 nm^3 compared with $.027\text{ nm}^3$ for the B2 TiPt compound. This suggests that the faulted phase contains somewhere around 96 atoms per unit cell.
4. Since there are additional phases present in this portion of the phase diagram, we made preliminary attempts to analyze an as-cast structure of an intermediate Ti-34Pt alloy. The solidification structure was complex and

the arrangement of the phases was used to speculate on the nature of the phase diagram, i.e., how the phases are related to one another. Attempts were also made to homogenize this material in order to determine what phases are stable at this temperature and composition. It was found that the homogenization kinetics are extremely sluggish, i.e., holding it for 114h at 1200°C caused some spheroidization but the structure still had not attained equilibrium. This indicates that the diffusivity of Pt in these alloys is extremely slow.

5. A fourth new phase with a Ti:Pt ratio of ~4 was observed in the binary Ti-34Pt alloy. This phase is cubic ($m3m$ point group) with a lattice constant of around 0.8nm. Based on the composition, morphology, location and volume fraction of this phase in the microstructure, it was speculated that it must be an interstitial compound. Unfortunately, our attempts to use electron energy loss spectroscopy to determine if interstitial elements are present have been unsuccessful to date.

The importance of these analyses lies in the observations that one or more of these secondary phases is present in essentially all of the binary, ternary and higher order alloys studied. Thus, as the property data base is developed, it will be important to understand the role of these minor phases. Unlike the Nitinol alloys that are used near room temperature, these alloys will experience considerably higher temperatures and, therefore, microstructural stability (particle coarsening, grain growth, etc.), creep behavior, oxidation behavior, impact resistance, etc. are important and may be influenced somewhat by these phases. If indeed this is the case, it is necessary to know their identities and the regimes in which they form given that some will probably be less desirable than others.

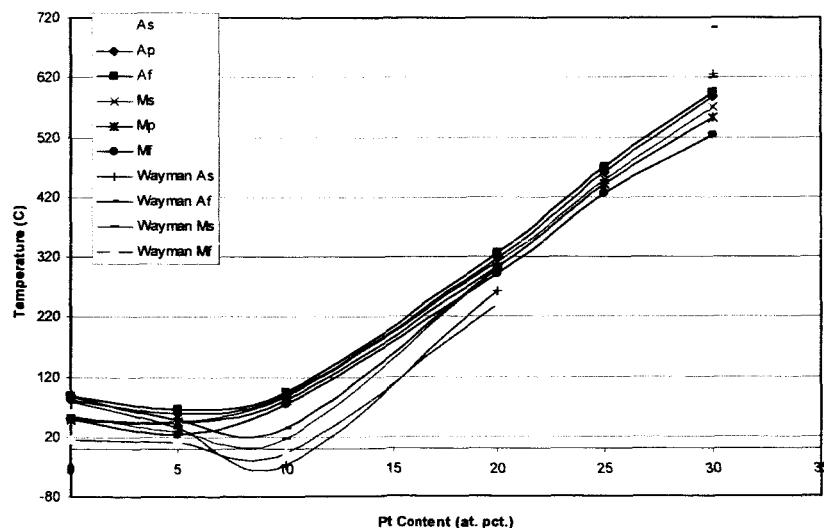


Figure 1. Transformation temperatures of current alloys along with those from the study by Lindquist and Wayman. A corresponds to the austenite phase, M to the martensite; the subscripts s, p and f correspond to the start, peak and finish temperatures, respectively.